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LA-5062-PR ✓

PROGRESS REPORT

CMB-13 Research on Carbon and Graphite

Report No. 20

Summary of Progress from November 1, 1971 to January 31, 1972



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This report presents the summary of progress of CMB-13 research on carbon and graphite at LASL. The four most recent reports in this series, all unclassified, are:

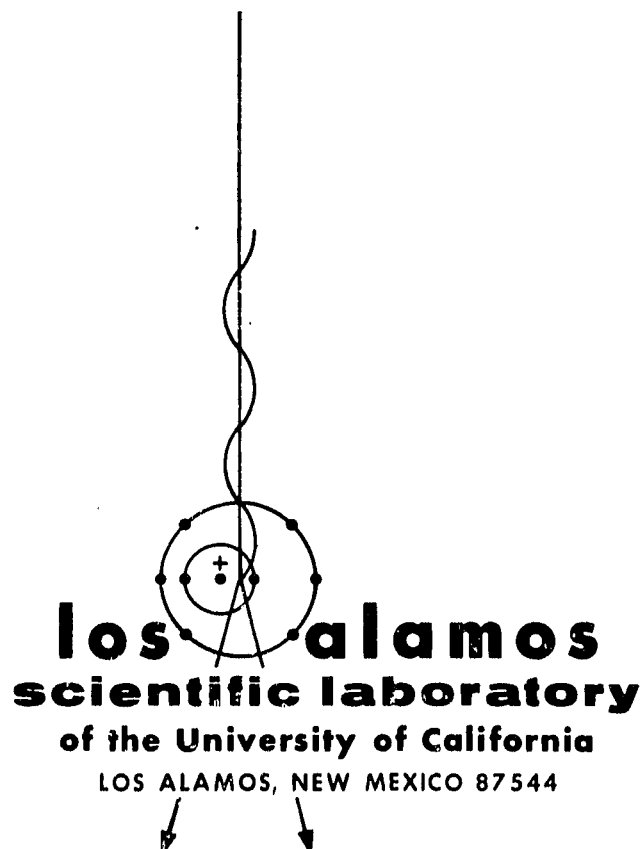
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LA-5062-PR
Progress Report
SPECIAL DISTRIBUTION
ISSUED: October 1972

CMB-13 Research on Carbon and Graphite

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by
Morton C. Smith

Supported in part by the Office of Advanced Research and Technology
of the National Aeronautics and Space Administration.

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CMB-13 RESEARCH ON CARBON AND GRAPHITE

REPORT NO. 20: SUMMARY OF PROGRESS FROM NOVEMBER 1, 1971 TO JANUARY 31, 1972

by

Morton C. Smith

I. INTRODUCTION

This is the twentieth in a series of progress reports devoted to carbon and graphite research in LASL Group CMB-13, and summarizes work done during the months of November and December, 1971, and January, 1972.

It should be understood that in such a progress report many of the data are preliminary, incomplete, and subject to correction, and many of the opinions and conclusions are tentative and subject to change. This report is intended only to provide up-to-date background information to those who are interested in the materials and programs described in it, and should not be quoted or used as a reference publicly or in print.

Research and development on carbon and graphite were undertaken by CMB-13 primarily to increase understanding of their properties and behavior as engineering materials, to improve the raw materials and processes used in their manufacture, and to learn how to produce them with consistent, predictable, useful combinations of properties. The approach taken is microstructural, based on study and characterization of natural, commercial, and experimental carbons and graphites by such techniques as x-ray diffraction, electron and optical microscopy, and porosimetry. Physical and mechanical properties are measured as functions of formulation, treatment, and environmental variables, and correlations are sought among properties and structures. Raw materials and manufacturing techniques are investigated, improved, and varied systematically in an effort to create specific internal structures believed to be responsible

for desirable combinations of properties. Prompt feedback of information among these activities then makes possible progress in all of them toward their common goal of understanding and improving manufactured carbons and graphites.

Since its beginning, this research has been sponsored by the Division of Space Nuclear Systems of the United States Atomic Energy Commission, through the Space Nuclear Propulsion Office. More recently additional general support for it has been provided by the Office of Advanced Research and Technology of the National Aeronautics and Space Administration. Many of its facilities and services have been furnished by the Division of Military Application of AEC. The direct and indirect support and the guidance and encouragement of these agencies of the United States Government are gratefully acknowledged.

II. RAW MATERIALS

A. Phenolic Resin Binders (E. M. Wewerka)

Although they have not so far been used for either purpose by LASL Group CMB-13, phenolic resins have reportedly been used successfully elsewhere both as binders and as impregnants for the manufacture of carbons and graphites. They appear to have certain advantages in both applications. An investigation of their synthesis and general usefulness has therefore been undertaken.

Phenolic resins are used in two different forms, both of which are prepolymers requiring further treatment to effect crosslinking. These are identified as the resol form and the novolak form.

Novolaks are made by polymerizing an excess of phenol with formaldehyde, usually in the presence of an acid catalyst. The resulting polymer contains mainly phenolic groups at the chain-ends. Polymers of this type are relatively stable and have good shelf lives. To cure them, additional formaldehyde is added to the novolak prepolymer which, under the influence of heat, then polymerizes further and crosslinks.

Resols are usually made by the base-catalyzed copolymerization of phenol and an excess of formaldehyde, so that the resulting polymer contains a predominance of terminal hydroxymethyl groups. They are normally converted to the fully crosslinked state by the application of heat alone. One disadvantage of resol prepolymers is that they are inherently reactive, and thus are relatively unstable when stored. However, they are convenient in not requiring additions of catalysts to cure them, and at least initially this investigation will not require a resin having long shelf life. Accordingly, the resols have been selected for the preliminary CMB-13 studies.

After a short developmental period five experimental resols were synthesized from reactant mixtures containing a 2.5 to 1 molar excess of formaldehyde. The resins produced differ from each other principally with regard to initial degree of polymerization, and vary in viscosity from about 1000 cp to 100,000 cp. They will be characterized particularly with regard to the proportions and graphitizing behaviors of their carbon residues, and may eventually be used in fabrication and impregnation experiments.

B. POCO Coke Flour (L. S. Levinson)

A sample of a commercial coke filler produced by POCO Graphite, Inc., was obtained from LASL Group CMB-6, and has been examined by electron microscopy. It had been calcined only to 1000°C, so that its internal structure was very poorly developed. It consisted of substantially equiaxed particles ranging in size from sub-micron to about 100 μ diameter. The larger particles contained small, somewhat angular voids, most of which were in the size range 2 to 5 μ and were about 5 to 25 μ apart. The smaller particles were generally solid and free of internal voids, suggesting that -- as would be

expected -- fracture paths during grinding of the coke had propagated preferentially from one void to the next.

III. FABRICATION

A. Soaking-in of the Binder (H. D. Lewis)

As was discussed in Report No. 17 in this series, it has previously been observed that simply storing a resin-bonded raw mix for a few days before extruding it significantly improved the properties of the finished graphite. This was assumed to result from slow absorption of the binder into the surface-connected porosity of the filler.

To investigate this effect further, the series of graphites listed in Table I was manufactured from mixes designated ADK7 through ADK14. Each mix contained, by weight, 85 parts of CMB-13 Lot G-18 (Great Lakes grade 1008-S) graphite flour; 15 parts of Lot TP-4 Thermax carbon black; and 27 parts of furfuryl alcohol resin binder (Varcum 8251, containing 4% maleic anhydride curing catalyst). Mixes ADK7 and ADK14 were extruded immediately after blending. The other mixes were stored at room temperature in closed containers for periods of 24, 48, 76, 96, 164, 168 and 192 hours before extrusion. Periodic checks of the weights of the mixes indicated that no measurable weight loss occurred during storage. The mixes were extruded as 0.5-in. diameter rods at rates varying from 164 to 180 in./min. The extruded rods were cured to 200°C in a 66-hr cycle, and baked to 900°C in a 44-hr cycle. Graphitization was to 2800°C in a 24-hr cycle.

Bulk density and electrical resistivity were measured on the finished graphites to determine the effectiveness of the various soaking treatments. Results are summarized in Table II and plotted in Fig. 1. Specimens ADD8 and ADK1 were made by J. M. Dickinson and were discussed in Report No. 17.

The data trends shown in Fig. 1 indicate that an improvement in properties of the finished graphite can indeed be expected to result from soaking the mix for 192 hours (approximately one week) prior to extrusion. The consistency of the bulk density values for specimens ADD8, ADK1, and ADK9, which were soaked for 168 and 164 hours, is considered to indicate the reproducibility

TABLE I
ADK GRAPHITES - EXTRUSION CONDITIONS

Specimen Number	Soaking Time		Pressure psi	Velocity in./min	Vacuum Torr	Temperature, °C		Green Dia in.	Remarks ^(d)
	Days	Hours				Mix	Chamber		
ADK-7	0	0	7830	168	350	45	45	.506	Straight
ADK-13	0	0	7200	171	350	39	45	.502	Slight bow
ADK-12	1	24	6750	171	350	41	45	.502	Slight bow
ADK-10	2	48	8540	164	350	40	48	.501	Slight bow
ADK-11	3-1/16	76	7830	171	325	40	45	.502	Slight bow
ADK-4	4	96	12150	159	350	46	45	.506	Slight bow
ADK-9	6-5/6	164	9000	167	325	40	45	.501	Slight bow
ADD-8 ^(a)	7	168	7650	171	700	42	45	.503	---
ADK-8	8	192	9630	171	350	41	45	.501	Straight
ADK-1 ^(b)	7	168	---	164	1000	45	40	.504	---
ADK-14 ^(c)	8	192	6840	180	350	38	45	.502	Bow

(a) Extrusion representing Dickinson's first observation of the effect of "soaking-in" of binder (LA-4770-MS).

(b) Dickinson's repeat of the ADD-8 experiment (LA-4770-MS).

(c) Extruded immediately after blending; rods covered and "soaked" 192 hours prior to cure.

(d) Rods indicated showed slight bow (approx. 1/32 in. bow in 7-1/2 in. length). ADK-14 rods showed approx. 1/16 to 3/32 in. bow in 7-1/2 in. length, and thumbnail-shaped surface defects from roughness in runout-table groove.

TABLE II
PROPERTIES OF ADK GRAPHITES

Specimen Number	Soaking Time		Bulk Density g/cm ³	Binder Carbon Residue, %	Electrical Resistivity μ Ω cm
	Days	Hours			
ADK-7	0	0	1.861 ± .006 ^(d)	47.2 ± 0.2 ^(d)	1203 ± 16 ^(d)
ADK-13	0	0	1.863 ± .002	45.3 ± 0.2	1245 ± 7
ADK-12	1	24	1.882 ± .001	46.4 ± 0.2	1138 ± 5
ADK-10	2	48	1.895 ± .003	46.6 ± 0.2	1143 ± 10
ADK-11	3-1/6	76	1.886 ± .002	46.4 ± 0.1	1117 ± 3
ADK-4	4	96	1.876 ± .001	48.6 ± 0.3	1169 ± 16
ADK-9	6-5/6	164	1.894 ± .002	46.2 ± 0.2	1154 ± 8
ADD-8 ^(a)	7	168	1.899 ± .003	47.1 ± 0.2	1079 ± 9
ADK-8	8	192	1.899 ± .002	47.7 ± 0.1	1118 ± 5
ADK-1 ^(b)	7	168	1.894	45.7	1128 ± 9
ADK-14 ^(c)	8	192	1.878 ± .003	44.1 ± 0.4	1189 ± 11

(a), (b) Dickinson's experiments on effect of "soaking-in" of binder (LA-4770-MS).

(c) Extruded immediately after blending; rods covered and "soaked" 192 hours prior to cure.

(d) Variability in measured values reported as ± one standard deviation.

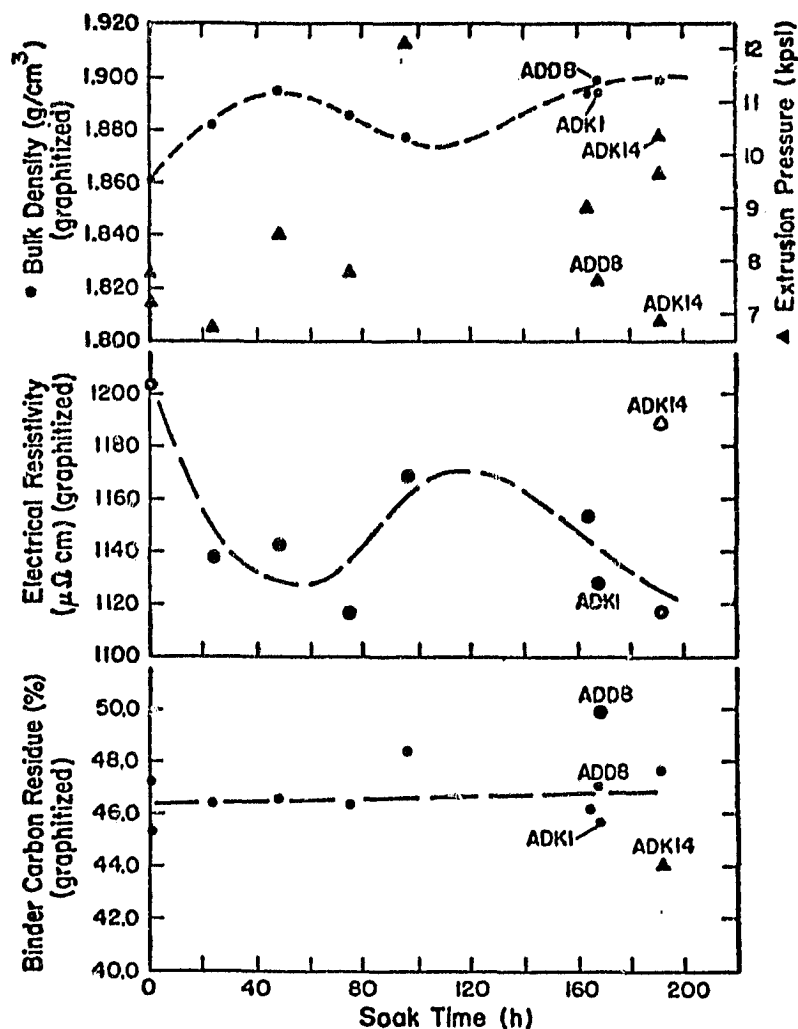


Fig. 1. Effect of pre-extrusion soaking time on density, extrusion pressure, electrical resistivity, and carbon residue.

of the experiment. Good reproducibility is also indicated by the density values for specimens ADK7 and ADK13, which were not soaked before extrusion and which were manufactured about four weeks apart. If it is assumed that the "scatter" in bulk density data is of the order of the difference between the values for ADD8 and ADK1, then the shape of the bulk density vs soaking time curve in Fig. 1 is realistic, and indicates a complex effect of the pre-soak on the rheology of the extrusion mix. The points on the bulk density and extrusion-pressure plot representing the 96-hour soak could be outliers, resulting from some unknown process perturbation, and additional experiments should probably be performed using soaking times of 96 hours and between 100 and 160 hours.

A conjectural mechanism can be offered to explain the effects of pre-extrusion soaking time on the density and resistivity of the finished graphite. It seems reasonable to assume that, during storage, the binder is slowly adsorbed onto particle surfaces and absorbed into surface irregularities and surface-connected voids. This

more extensive wetting of particles and filling of their surface roughness may reduce interparticle friction, permitting the particles to move into closer-packed arrays during extrusion, and thus increasing packing density as well as effectively increasing the densities of individual filler particles. If the effect of closer packing were to increase "squeeze-out" of the binder, this would tend to compensate for increased residence time of pyrolysis gases, and keep the proportion of binder-carbon residue nearly constant -- as appears to be the case. A minimum in the density curve and a maximum in the resistivity curve might be explained on the basis of the rates of short-range diffusion into particles and longer-range diffusion between them. If the lower molecular-weight species in the binder are adsorbed onto particle surfaces and absorbed into surface irregularities during the first few hours of soaking, the effects would be to reduce interparticle friction, produce a closer-packed particle array, increase particle density, and thus increase bulk density and electrical conductivity. Because of the wide spectrum of interparticle void sizes, continued soaking might then deplete the binder -- or the low molecular weight species in it -- in certain localized regions where the surface area of particles was high and the supply of binder was small, thus increasing average interparticle friction and overall mix viscosity. This "drying out" of the mix, which appears to occur, would reduce packing efficiency and final bulk density. Finally, with still longer pre-soaking, the binder would have time to diffuse into depleted regions and to equilibrate throughout the mix with regard to the concentration of various molecular species. The results would finally be a reduction in interparticle friction, better packing, increased bulk density, and reduced electrical resistivity. This speculative mechanism, then, involves a rather complicated combination of the diffusional characteristics of various molecular species in the binder, changing interparticle friction, and decreasing intraparticle porosity.

Whatever the mechanisms involved, it appears that pre-soaking a resin-bonded extrusion mix for periods as short as 2 days significantly improves the properties of the finished graphite. Some of this improvement may be

lost if soaking is continued for an additional 1 to 3 days, but it is apparently restored and perhaps enhanced if the total pre-soaking time is increased to about one week.

B. Scaling-up of the Hot-Molding Operation (R. J.

Imprescia)

Hot-molded experimental graphites are now commonly made by CMB-13 in the form of cylindrical billets approximately 2.75-in. in diameter. To examine the problems involved in scaling up this manufacturing operation, a billet approximately 8-in. in diameter and 4.5-in. high was made from a mix composition identical to that previously used to mold a standard (2.75-in. dia) specimen. The mix contained 100 parts of a non-needle coke filler, CMB-13 Lot C-8, and 33 parts of grade 30M coal-tar pitch. The total weight of the die charge used to make the larger billet was approximately 17 lb, and manufacturing processes were as nearly as possible identical with those previously used to make the small one.

The mix for the large billet (Specimen 81A-2) was prepared by standard solvent-blending and hot-chopping methods. It was hot-molded at 2000 psi in a graphite die which was heated in a 24-in. diameter induction furnace. After molding the billet was removed from the die, weighed and measured, replaced in the die, and graphitized in the same induction furnace to approximately 2400°C. Because of difficulties in controlling temperature manually, heating rates were not as uniform as was planned. The approximate heating cycles for molding and graphitizing were:

Molding:

RT to 80°C at 1.6°C/hr
80 to 225°C at 6.0°C/hr
225 to 480°C at 9.8°C/hr
480 to 735°C at 21.0°C/hr
735 to 830°C at 6.8°C/hr
830 to 1145°C at 39.0°C/hr

Graphitizing:

RT to 1480°C at 85°C/hr
1480 to 2030°C at 265°C/hr
2030 to 2400°C at 300°C/hr

The density and shrinkage properties of Specimen 81A-2 are compared in Table III with those of Specimen 79I-1, a 2.75-in. diameter billet previously made from an identical mix in a similar manufacturing procedure. The agreement between the two sets of properties is considered to be very good.

C. Glass-Like Carbons (E. M. Wewerka, R. J.

Imprescia, H. D. Lewis)

The commercial glass-like carbons are nearly amorphous materials which typically have very high hardness, strength, and elastic moduli, and very low permeabilities to liquids and gases. Very little information is available on the raw materials and manufacturing processes used to produce them. It is believed, however, that the commercial glass-like carbons are normally produced from thermosetting resins which have been cured and baked in very long heat-treating cycles.

To elucidate the important variables in the production of glass-like carbons, a series of experiments has been undertaken using furfuryl alcohol resins as precursor materials. In the initial experiments, two such resins differing widely in rheological characteristics have been used: EMW-302, a standard, acid-polymerized, CMB-13 resin, with viscosity of 420 cp; and a "1600 pot-residue" resin made by distilling the volatile material from a standard, acid-polymerized, 1600-cp resin at 180°C under reduced pressure. The pot residue had very high viscosity, having the consistency of thick tar at room temperature. Specimens of each, with and without additions of a curing catalyst, were made by casting 20.0-g samples of the resin into a 100-ml beaker, producing a disk about 3/8-in. thick and 1.5-in. diameter. Castings made from the EMW-302 resin were poured at room temperature. Those made from the 1600 pot-residue were poured at 75°C. All samples were then cured by heating to 200°C over a 13-day period.

The conditions of the various samples after curing are indicated in Table IV. The uncatalyzed samples showed numerous wrinkles and cracks. All samples catalyzed with maleic anhydride were badly expanded or cracked. However, all samples catalyzed with QX-260 appeared to be dense, crack-free, and uniform.

TABLE III
DENSITY AND SHRINKAGE PROPERTIES OF SPECIMENS 79I-1 AND 81A-2

	Specimen Number	
	79I-1	81A-2
Calculated Binder Optimum, pph	21.0	20.7
Binder Residue, %	46.3	46.1
Packed Filler Density, g/cm ³	1.535	1.539
Bulk Density, Baked, g/cm ³	1.770	1.773
Bulk Density, Graphitized, g/cm ³	1.842	1.850
Dimensional Chg., Baked to Graph., %		
Δl	-3.0	-2.8
Δd	-2.0	-2.0
Δv	-6.8	-6.7

TABLE IV
GLASS-LIKE CARBON CASTINGS

Sample No.	Resin	Catalyst	Catalyst Conc. Wt. Percent	Sample Integrity After Curing
GC-1	1600 Pot-Residue	Maleic Anhydride	5	Puffed and porous
GC-2	1600 Pot-Residue	QX-260 ^(a)	5	No cracks or pores
GC-3	1600 Pot-Residue	None	-	Puffed and porous
GC-4	1600 Pot-Residue	QX-260	1	No cracks or pores
GC-5	1600 Pot-Residue	Maleic Anhydride	1	Very porous; cracked
GC-6	EMW-302	QX-260	5	No cracks or pores
GC-7	EMW-302	Maleic Anhydride	5	Cracked and puffed
GC-8	EMW-302	None	-	Surface puffed and wrinkled

(a) QX-260 is an experimental curing catalyst supplied by the Quaker Oats Co.

One of the samples catalyzed with QX-260, after curing, was baked in a standard heating cycle, requiring 72 hr to reach 900°C. It broke up badly. A second sample was then baked to 900°C in a much slower cycle, requiring 21 days. It too cracked badly during baking.

Additional samples identical in composition with specimen GC-2 (the 1600 pot-residue, catalyzed with 5% QX-260) were cast and cured in a relatively rapid cycle requiring 3 days to reach 200°C. All survived this faster curing cycle without apparent damage.

From these preliminary results it was concluded that the addition of a curing catalyst is important to the

production of sound castings of a furfuryl alcohol precursor resin for the production of a glassy carbon, and that QX-260 is a better catalyst for this purpose than is maleic anhydride. It was also concluded that extremely slow baking treatments are probably required to prevent damage to the sample from shrinkage and gas evolution during pyrolysis of the cured resin. (This is consistent with the 4- to 5-month baking times said to be used by commercial producers of glass-like carbons.)

With this background, experiments have been undertaken intended eventually to lead to the production of relatively thick glass-like carbon sections in the shortest

possible manufacturing cycle. Three CMB-13 furfuryl alcohol resins have been selected for this purpose, with viscosities of 400, 7500, and 50,000 cp. Samples of each have been catalyzed with 1% and with 5% additions of QX-260, and cast into 0.5-in. dia by 4-in. long Pyrex test tubes. Samples of each will be cured to 200°C in 3-day and 12-day cycles, both at atmospheric and at reduced pressure. Those which are intact after curing will be baked to 900°C in an argon atmosphere in 1-month, 2-month, and 4-month cycles, and at reduced pressure in a 2-month cycle. Samples which appear to be sound after baking will finally be graphitized to 2800°C in a normal cycle.

IV. PARTICLE PACKING

(H. D. Lewis, W. M. Visscher, A. Goldman)

As has previously been reported, a study of the particle packing problem has been undertaken and is continuing. Its principal purposes are, if possible, to determine the characteristics of the arrays produced by packing heterogeneously sized particles, and to determine whether some combination of size-distribution parameters can be used to predict the packing efficiencies of particulate systems. Recent efforts have been directed toward completing the study of the one-dimensional analytical model and continuing the study of two- and three-dimensional models, using Monte Carlo methods.

It is evident that a one-dimensional model represents a serious oversimplification of the three-dimensional packing problem. It has, however, been used to test the effect on packing efficiency of changing the coefficient of variation ($CV_d = \sigma_d/\mu_d$) of the particle-size distribution. An integral equation derived by Visscher -- and discussed below -- was used to predict packing efficiency, and appeared to indicate that packing fraction was a monotonically increasing function of CV_d . The packing fraction obtained for an array of monosized particles on a line was 0.748, which is the value previously obtained by Ney (Ann. Math. Stat., 33, 702, 1962), Renyi (Publ. Math. Inst. Hung. Acad. Sci., 3, 109, 1959), Blaisdell and Solomon (Tech. Rept. No. 148, Dept. Stat., Stanford University), and others. However, for more

complicated particle-size distribution functions, nonsense values of packing fraction were often obtained. It was then discovered that the method of calculating packing fraction from the integral equation was in error.

Visscher's integral equation for the one-dimensional case is of the form

$$N(x) = \int_0^x g(d)dd \left[1 + \frac{2}{x-d} \int_0^{x-d} N(t)dt \right]$$

where: $N(x)$ = number of particles or segments packed ("parked") on the line;

x = length of line on which segments are placed;

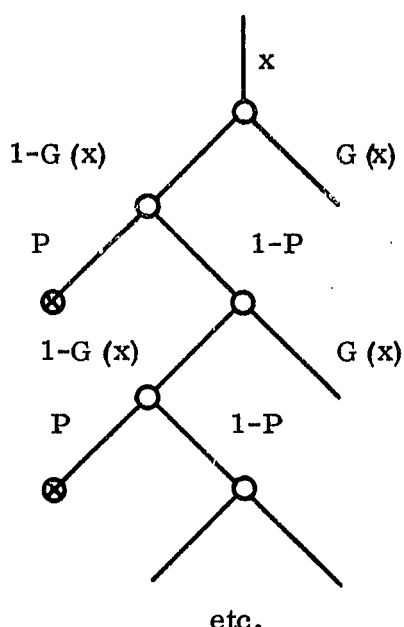
$g(d)$ = probability-density function of lengths of segments;

d = segment length.

From the solution to this equation, the packing fraction was calculated to be $N(x)\bar{d}/x$, where \bar{d} is the average segment length. However, as was the case with Ney's solution, the resulting estimate of packing fraction was in error because, for all but the monosized case, the realized distribution of particles on the line was not the same as the initial distribution from which the particles were randomly selected -- i.e., the wrong value of \bar{d} was being used.

Visscher therefore modified his analytical solution to the one-dimensional particle-packing problem in such ways that the mean of the realized distribution (i.e., the mean of the particle-size distribution actually placed on the line), as well as the higher moments, could be computed and used to estimate packing fraction. He also introduced the concept of a "termination probability" for occupation of spaces on the line. This deals with the possibility that a particle may be selected which is too large to fit into an unoccupied space on the line -- the space being bounded by two particles already in place on the line. The question is whether this space should be considered permanently occluded by the oversize particle, forming a packing defect, or whether instead there is some specific probability that the space will subsequently be filled by a smaller particle. The general "parking" method used to account for this possibility is to begin by

placing the first segment of length d in $x > d$. Each successful "park" then generates a branch, as indicated in the diagram below.



Here $G(x) = \int_0^x g(d) dd$. If $x > d_{\max}$, another segment

is parked. If $x < d_{\min}$, the branch is terminated according to the rule: if $d_{\min} < x < d_{\max}$, pick a segment from the distribution represented by $g(d)$; if $d < x$, place the segment on the line; if $d > x$, terminate the branch with probability P , and with probability $(1-P)$ pick another segment d' ; if $d' < x$, place it on the line x .

The net probability of success in parking, $Y(x)$, can be shown to be the sum of a geometric series,

$$Y(x) = \frac{G(x)}{1 - [1 - G(x)][1 - P]}.$$

The new integral equation to be solved numerically is then

$$N(x) = Y(x) \left[1 + \frac{2}{G(x)} \int_0^x \frac{g(d) dd}{x-d} \int_0^{x-d} N(x') dx' \right].$$

For $P = 1$, $Y(x) \rightarrow G(x)$, and for $P = 0$, $Y(x) \rightarrow 1$.

When $P = 1$, the new equation reduces to the old integral equation.

This new analytical solution was used to determine the packing fraction for binary combinations of monosized systems having various mixing fractions and size ratios.

For the monosized case it gave the same packing fraction, 0.748, previously calculated. However, coefficient of variation did not seem to be a reliable indicator of a maximum in packing fraction, and it was questioned whether examination of binary mixtures of monosized systems represented a reasonable particle-packing analog.

Visscher's computer program was therefore modified by Lewis and Goldman so that particle-size selection could be made using distribution functions analogous to the "old" analytical solution programs. At present, results are available only for the uniform size distribution. These results are shown in Fig. 2, and obviously differ from the results of the old program. Intuitively, it is reasoned that termination probabilities between 0.0 and 0.5 are more likely to represent actual packing of heterogeneously sized system than are higher probabilities -- i.e., that a packing defect formed initially has a greater than 0.5 probability of being entered subsequently by a smaller particle. Therefore the upper three curves of Fig. 2 are probably the ones of greatest interest.

Meanwhile, Visscher has written a Monte Carlo program to simulate packing of circles in a two-dimensional container. The first experiment using this program consisted of dropping circles into the container, each circle being dropped along the same line passing through the center of the first circle deposited. It was assumed that each particle maintained contact with the surfaces of particles previously deposited; i.e., particles did not bounce or rebound, and rolled until a "low-energy" position formed by two or more near-neighbor particles and/or the container boundary was encountered. The resulting array had the configuration of the basal plane of the close-

packed hexagonal crystal structure, with a two-dimensional packing fraction of 0.903. A second similar experiment using a binary mixture of circles, with a diameter ratio of 3:1, a mixture fraction of 0.5, and a random selection of drop sequence, gave a disordered geometric array and a packing fraction of 0.837. Several other

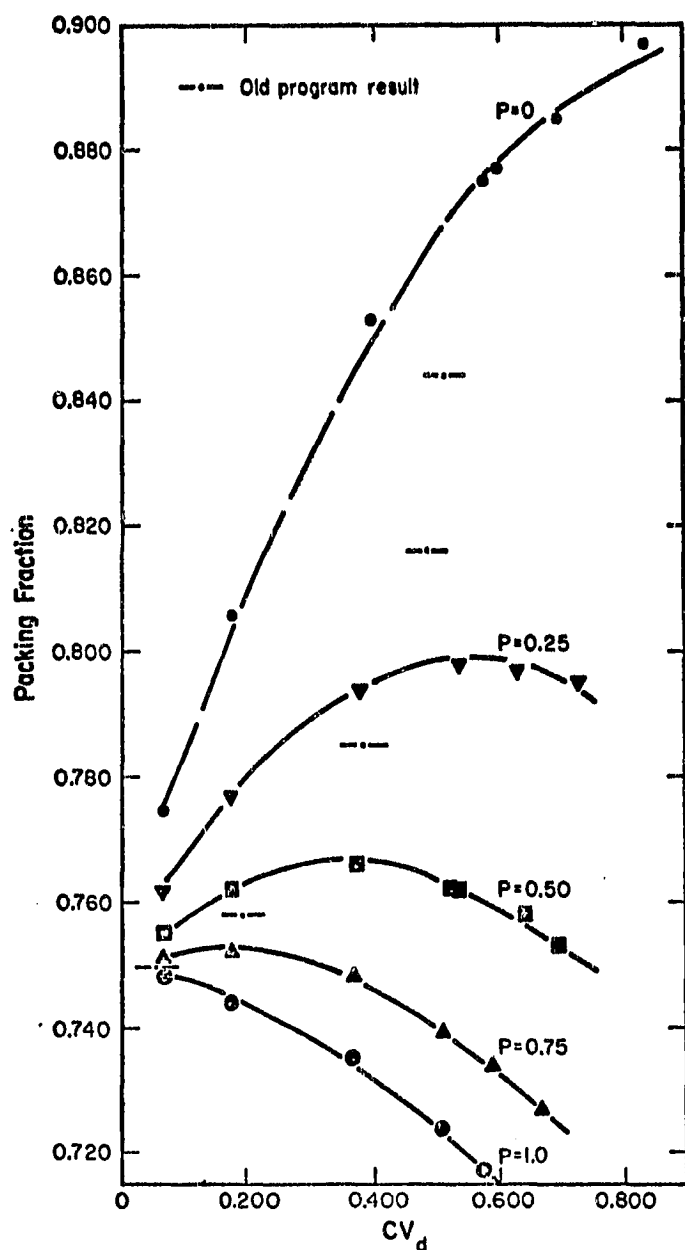


Fig. 2. Relation between packing fraction and CV_d for various termination probabilities, P . Uniform segment-size distribution.

experiments were run in which periodic boundary conditions were imposed on the container -- e.g., the container was a cylindrical surface, and random drop position was permitted for each small circle dropped into it. In all cases the packing fraction was less than 0.903. These results would be expected from the observed disordering effect of random introduction of balls of a different size into a three-dimensional close-packed array. Fig. 3 is one two-dimensional array generated by the Monte Carlo program for a mixture of circles having 2:1 diameter ratios. It appears to be realistic for the system considered. It can be argued, however, that it is not realistic for an actual particle system in which, for example, the larger circles have a small but finite variance of

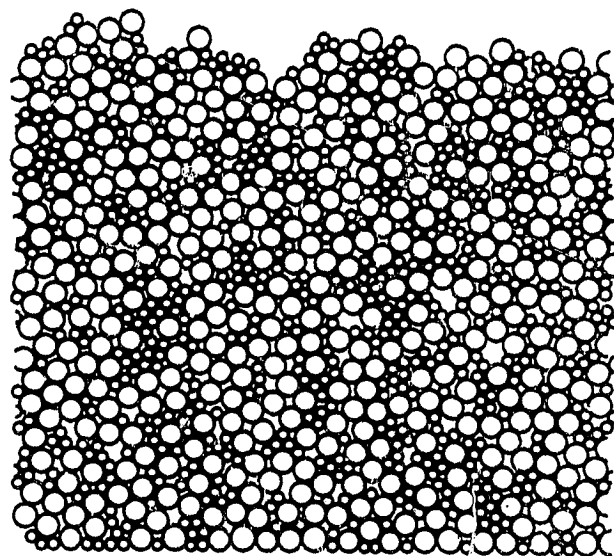


Fig. 3. Computer model of two-dimensional array of circles.

diameters, and are therefore incapable of close packing in the crystallographic sense. In this case, packing might be improved by adding some proportion of circles having a much smaller mean diameter, again with a finite variance of sizes. Experiments along these lines are under way, in an attempt to model the effect of introducing "fines" into a mass of coarse particles.

With A. M. Bolsterli, LASL Group T-9, Visscher has just completed a Monte Carlo program to simulate random packing in a three-dimensional container having periodic boundary conditions. To check the program, an experiment was run in which monosized spheres were dropped in the direction normal to a plane on which similar spheres had been preplaced in the centered hexagonal pattern of the basal plane in a close-packed hexagonal structure. The result was the ABAB... stacking of the close-packed hexagonal array, with a three-dimensional packing fraction of 0.74. Other experiments using heterogeneously sized balls and various constraints on ball interactions are now under way.

V. PUBLICATIONS RELATING TO CARBONS AND GRAPHITES

Smith, M. C., "CMB-13 Research on Carbon and Graphite, Report No. 19, Summary of Progress from August 1 to October 31, 1971," Los Alamos Scientific Laboratory Report No. LA-4917-PR, March, 1972.

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1 / 22 / 73